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AUTHOR(S): Lynda M. Faires
Byron A. Palmer
Paul T. Cunningham

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Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

ANALYTICAL APPLICATIONS OF ICP-FTS

Lynda M. Faires, Byron A. Palmer, Paul T. Cunningham
Analytical Chemistry Group, Chemistry Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

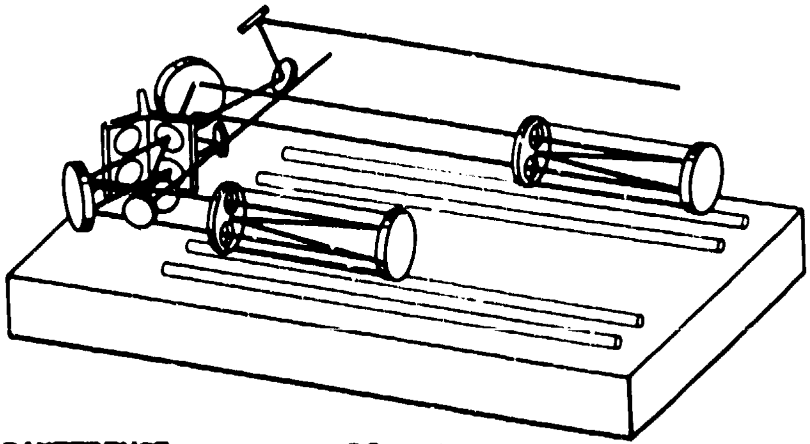
Abstract

The Analytical Chemistry Group of the Chemistry Division at Los Alamos National Laboratory has been investigating the analytical utility of the inductively coupled plasma (ICP) - Fourier transform spectrometer (FTS) combination. While a new state-of-the-art FTS facility is under construction at Los Alamos, preliminary data has been obtained on the one-meter FTS at the National Solar Observatory at Kitt Peak, Arizona. This paper presents an update of the Los Alamos FTS facility, which is expected to be completed in 1986, and presents data showing the analytical potential of an ICP-FTS system. Some of the potential problems of the multiplex disadvantage are discussed, and the advantages of the high resolution obtainable with the FTS are illustrated.

Fourier transform spectrometers have the potential of fulfilling many of the criteria of an ideal detection system for analytical atomic spectroscopy. They have the ability to provide comprehensive and simultaneous wavelength coverage over a selected spectral bandpass. This bandpass may be varied by optical and electronic filtering over the range from the ultraviolet to the far infrared and may be quite broad or quite narrow in scope. In this respect, Fourier transform spectrometers resemble the use of photographic detection techniques, but they also include the further advantages of very high accuracy of both the wavelength and the intensity measurements. These features are combined with high and variable resolution. The resolution obtained depends on the extent of the mirror movement in the interferometer, and full resolution of most UV-VIS emission lines in the ICP, for example, can be achieved with an optical path difference of 10-20 cm. This resolution can be varied to suit the analytical or experimental problem simply by varying the mirror movement. The large intensity dynamic range and high optical throughput of FT instruments make them suitable for spectrochemical measurements. And their computer compatability makes data management easily adapted to modern trends in computerization of the analytical laboratory.

Historically, Fourier transform spectrometers have been developed and used for applications in the infrared region of the spectrum. In deed, they have become instruments of choice for most IR spectroscopy after a decade of FTIR development combined with rapid advances in the field of computers. The major causes for the slower development of FTS in UV-VIS spectroscopy relate primarily to the more critical mechanical and optical tolerances required for interferometry at the shorter wavelengths, considerations related to free spectral range and aliasing, and the possible loss of the multiplex advantage in photon-noise limited situations. But advances in modern technology have now made development of UV-VIS Fourier transform spectrometers both possible and practical.

The Analytical Chemistry Group of the Chemistry Division of Los Alamos National Laboratory is currently engaged in the design and construction of a state-of-the-art high resolution Fourier transform spectrometer. Completion of this instrument is expected in early 1986. The Los Alamos FTS will have a 2.5 meter optical path difference (with the option of double-passing to 5 meters). The optical design consists of a folded Michelson interferometer with two cat's eye retroreflector mirror assemblies moving on oil bearings and translated by linear motors. There are two optical ports. The servo system will control the mirror position to within 0.3 nm. The beamsplitters are mounted on a rotating turret for easy interchange according to the spectral region being observed. The instrument will be capable of recording unaliased spectra over the entire range of 200 nm to 20 μm with wavenumber accuracy on the order of 0.0001 cm^{-1} and intensity accuracy on the order of 0.1%. The A/D converter consists of a 22-bit floating point converter with an array processor to digitally filter the interferogram. Extensive software is being developed to rapidly perform the large Fourier transforms (up to several million points) and process the spectral data into convenient formats. The optical design and specifications of the Los Alamos FTS are given in Figure 1. This instrument will provide the focus of a new facility which is expected to (1) enhance capabilities in analytical chemistry through the development of new and advanced techniques in spectroscopy (2) provide high resolution spectroscopic capabilities for the multifaceted needs of the Los Alamos National Laboratory and (3) operated partially in a user-facility mode available by proposal to both national and international scientists.



OPTICAL PATH DIFFERENCE	**2.5 meter** **(5.0 meter double pass)**
SPECTRAL RANGE	**200 nm - 20 μm** **(50000 - 500 cm^{-1})**
RESOLUTION	**0.002 cm^{-1}** **(0.001 cm^{-1} double pass)**
INTENSITY ACCURACY	**0.1%**
WAVENUMBER ACCURACY	**0.0001 cm^{-1}**
SCAN TIME (FULL RESOLUTION)	**4 min**

FIGURE 1

This laboratory has been involved for the past three years in exploring the potential of combining the inductively coupled plasma (ICP) excitation source for atomic emission spectroscopy with the Fourier transform spectrometer (FTS) as a detection system to produce a new technique: ICP-FTS. Preliminary experiments have been conducted using the one meter FTS located in the McMath Solar Telescope of the National Solar Observatory at Kitt Peak, Arizona. The designer of this instrument, Dr. J. W. Brault, has been a key consultant on the Los Alamos FTS project and has collaborated on the ICP-FTS studies. These experiments have demonstrated the potential of ICP-FTS both as a powerful diagnostic tool for spectrophysical studies of the ICP source and as a new method of analytical spectrochemical measurements.

ICP-FTS studies to date have included: the measurement of an excitation temperature vertical profile in the plasma [1], line width and line shape analysis [2], ICP emission characteristics in the IR to 2 µm [3] and beyond to 5 µm, the observation of high temperature molecular spectra such as OH and CN, assessment of the possibility of making new or improved measurements of atomic oscillator strengths [4], the recording of high resolution ICP wavelength tables [5] and reference spectra, the development of advanced analytical techniques [6,7], and studies of the noise characteristics of the ICP-FTS combination.

In order to assess the utility of ICP-FTS for analytical applications, working curves and detection limits have been established for several elements. In the cases where the same analytical UV wavelengths that are used in commercial wavelength-dispersive ICP spectrometers were accessible using the Kitt Peak FTS (which has an instrumental short wavelength cutoff at about 250 nm), detection limits by ICP-FTS were found to be comparable to those usually reported for ICP. In some cases however, it was necessary to use alternate and less sensitive lines for some elements, and the resulting detection limits were found to be somewhat higher, as expected. The Los Alamos FTS should have an instrumental cutoff of 200 nm or below in the UV, allowing the use of the most sensitive emission lines for ICP analysis. Working curves were found to be linear over the standard range of concentrations, with the exception of the alkali and alkaline earth elements which exhibit some self-absorption at concentrations in excess of 100 µg/ml. Typical working curves for the Al I 396.15 nm and the Ca II 393.37 nm lines are shown in Figures 3 and 4.

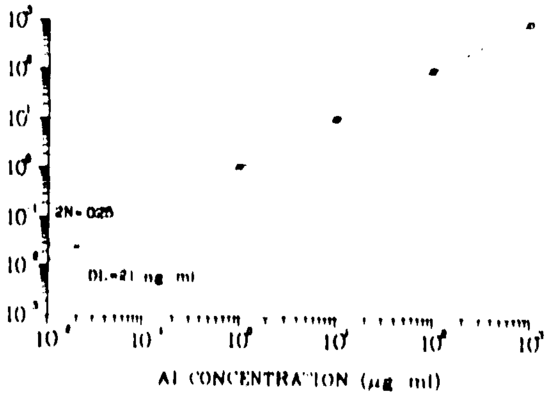


FIGURE 2

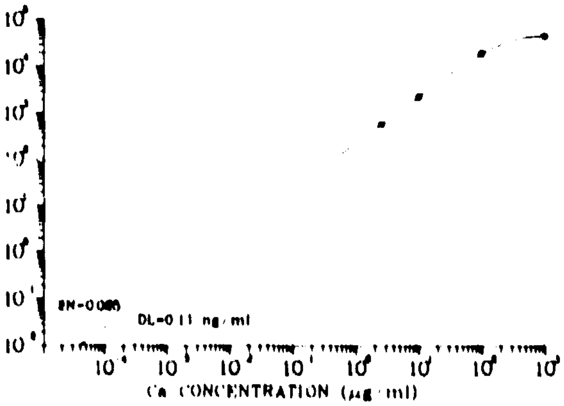


FIGURE 3

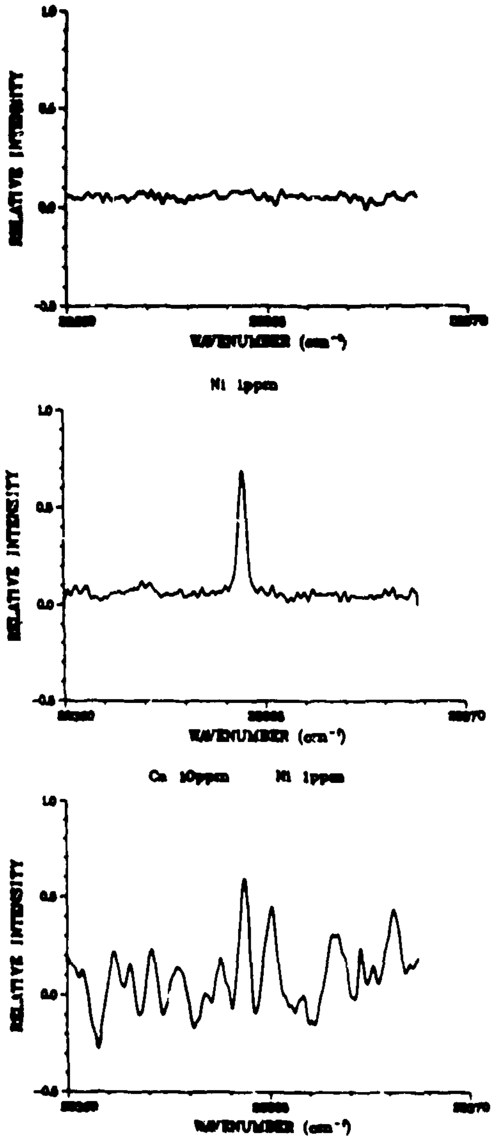


FIGURE 4

The calculation of detection limits by ICP-FTS requires some special consideration due to the multiplex nature of the spectrometer. Since all the emission intensity from the source falls on a single detector all the time during the measurement process, the total noise from the source will be distributed throughout the spectrum which results from the mathematical transformation, and each spectrum will have some different level of baseline noise depending on the particular composition of the sample. This baseline noise is measured as the standard deviation of the baseline intensity across a portion of the spectrum which does not contain any emission lines. In order for an emission line in the spectrum to be "detectable," it must have an intensity equal to some multiple (usually two, by definition) of the baseline noise. Since the baseline noise in a particular spectrum will depend on the total composition of the particular sample, then strong lines of matrix elements in the sample may increase the baseline noise of that spectrum and thereby degrade the detection limits for other analytes in the sample. This effect is called the multiplex disadvantage. Studies in this laboratory [6] predict that the "worse case" multiplex disadvantage will occur when alkaline earth elements are present as matrix elements in the samples. Transition metal elements at moderate concentrations do not cause such severe effects. Figure 4 illustrates a "worse case" example of the increase in spectral baseline noise in the presence of calcium matrix. In this figure, a portion of the spectrum centered around the Ni I 352.45 nm (28364.39 cm^{-1}) line is plotted on the same scale for direct comparison in each of the three cases. In the top figure, the spectrum of the blank solution shows the baseline noise level due to background emission of the ICP source. In the central figure, the Ni I line due to the 1 μg/ml Ni solution is clearly evident, and the baseline noise is not significantly different from that of the blank solution. In the bottom figure, the Ni I line due to 1 μg/ml Ni is still present at the same intensity as above, but now the presence of 10 μg/ml Ca has increased the baseline noise by a factor greater than 10 and therefore degraded the detection limits for Ni in the sample by the same factor.

Methods of overcoming this multiplex disadvantage problem and improving sensitivity for ICP-FTS in general are currently being explored. These methods include: (1) optical filtering and limited bandpass (2) post-FTS dispersion and multiple detectors (3) multiple line analysis (4) correlation techniques in both the Fourier and the frequency domains and (5) torch and nebulizer design to reduce source noise.

One of the most outstanding advantages of using Fourier transform spectrometers for ICP applications is the high resolution which is relatively easily attainable with those instruments. The resolution (in wavenumbers) is equal to 1/(2*optical path difference in cm). An optical path difference of 20 cm in the interferometer results in a resolution of 0.025 cm^{-1} which is equivalent to a resolution of 0.0002 nm at 300 nm. Since typical line widths of emission lines in the ICP are on the order of 0.003 nm [2], this is sufficient to <u>fully</u> resolve most emission lines in the source.

There are three obvious benefits of this result. First is the powerful information available for plasma diagnostics and studies of excitation mechanisms. Second is the reduction of spectral interferences in complex matrices such as actinides and rare earths to those interferences which are due to the natural linewidths themselves. Third is the ability to use high resolution, combined with the FTS accuracy in wavelengths and intensities, to generate a new set of standard reference tables for ICP emission [5].

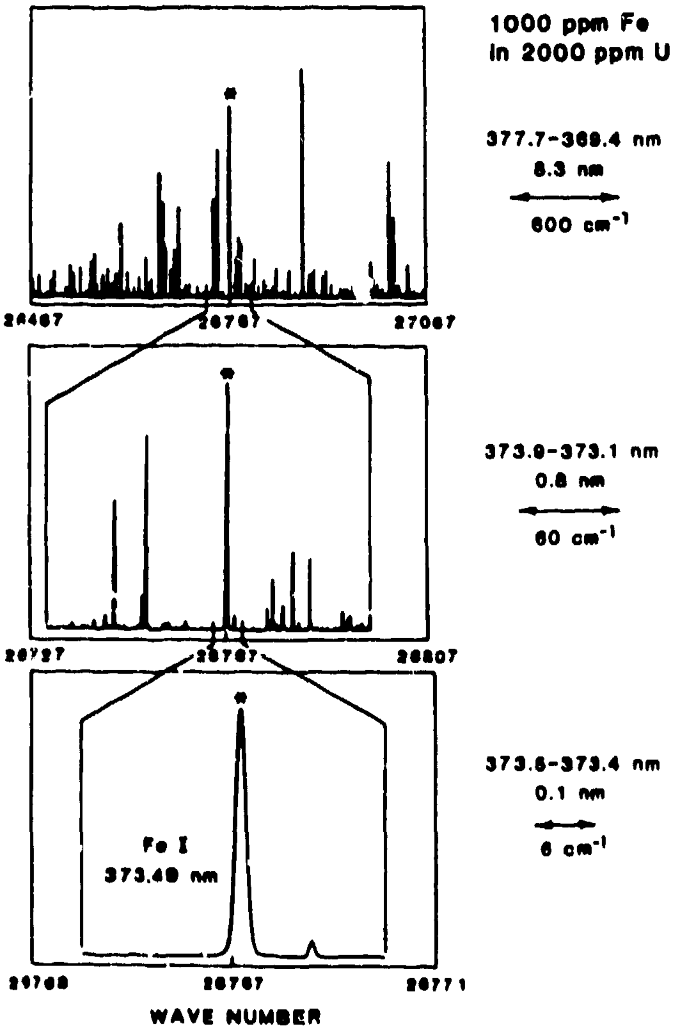


FIGURE 5

The ability of high resolution FTS to extract useful analytical lines out of extremely complex spectra is illustrated in Figure 5. Each segment shown here is from the same ICP-FTS spectrum of 1000 μg/ml Fe in 2000 μg/ml U. The top figure shows a 8.3 nm section containing dozens of strong and weak lines of both components. The middle figure shows the central 0.8 nm of the previous segment, plotted on an expanded scale. Now the individual lines are beginning to be distinquishable, but weak lines of U are seen to lie too close to the Fe lines to be resolved by conventional grating spectrometers. In the lower figure, the central 0.1 nm of the previous segment is again plotted on expanded scale, showing that the Fe I line at 373.49 nm is actually fully resolved from any U interferences and can be used for quantitative analysis without any corrections for spectral interferences and without any time consuming pretreatment or chemical separation steps performed on the sample before analysis. Similar successful resolution of many other analytical lines of several elements in the U matrix has been observed, and it is anticipated that the same advantage will be realizable in Pu matrix as well.

Summary

ICP-FTS promises to be an exciting and powerful new technique for spectrophysical and spectrochemical measurements. The multiplex characteristics of the FTS require special consideration in understanding and optimizing the analytical performance of ICP-FTS or in designing a FTS specifically for ICP applications. Comprehensive wavelength coverage, high accuracy of wavelengths and intensities, and high resolution are the outstanding features of FTS instruments for analytical atomic emission spectroscopy.

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